U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-267 774

Polynuclear Aromatic Content of Heavy Duty Diesel Engine Exhaust Gases

Gulf Research and Development Co, Pittsburgh, Pa

Prepared for

Coordinating Research Council, Inc, New York

17 Jan 77

PB 267 774

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22151

SECOND YEAR REPORT

ON

POLYNUCLEAR AROMATIC CONTENT OF HEAVY DUTY DIESEL ENGINE EXHAUST GASES

By

R. E. Spindt

Submitted To The
Coordinating Research Council, Inc.
CRC APRAC Contract CAPE-24-72
731CD004

January 17, 1977

Gulf Research & Development Company
P. O. Drawer 2038
Pittsburgh, PA 15230

TABLE OF CONTENTS

	Page No.
List of Tables	ii
List of Figures	iii
Abbreviations	iv
I Objective	1
II Summary	1
III Recommendations	3
IV Introduction	4
V Experimental Procedure	4
A. Engines & Fuels	4
B. PNA Sampling System Development	5
C. Distribution of Tracer in Sampling System	10
D. Solvent Selection for PNA Extraction From Soot	11
E. Analytical Procedures for PNA	14
1. Separation Steps	14
2. UV Spectrophotometry	16
VI Results and Discussion	22
A. Evidence for the Need to Redirect the Study Objective	22
B. PNA Emissions at No Load Operation	23
C. PNA Emissions at Half Load Operation	26
D. PNA Emissions at Full Load Operation	26
E. Effect of Sampling Time & Dilution on PNA Losses	28
References	30
Personnel	31
APPENDIX A - Analytical Procedure for PNA Hydrocarbons in Diesel Exhaust Gases	32
APPENDIX B - Data Summary	37

LIST OF TABLES

Table No.	Title	Page No.
I	PNA Hydrocarbon Recovered from Collection System in the Absence of Exhaust Gases	12
II	Analytical Recovery Validation of Four PNA Blended in Benzene	14
III	Effect of Solvent on PNA Recovery from Soot	15
IV	Reproducibility of Divided Sample Analyses	22
V	Effect of Sampling Time & Dilution Ratio on PNA Emissions at No Load, 1260 RPM in Mack Engine	24
VI	Effect of Sampling Time & Dilution Ratio on PNA Emissions at Half Load, 1260 RPM in Mack Engine	25
VII	Effect of Sampling Time & Sample Treatment on PNA Emissions at Full Load, 1800 RPM in Mack Engine	27
B1	Engine Experimental Data	38-41
B2	Test Fuel Inspection Data	42

LIST OF FIGURES

Figure No.	Title	Page No.
1	PNA Collection System in Use at End of First Year	6
2	PNA Collection System With Tracer Injection and Air Dilution Added	7
3	PNA Collection System With Modified Tracer Injector	8
4	Isocopic Tracer Injection System	9
5	Exhaust Gas Sampling System	13
6	Benzo (a) Pyrene Spectra	18
7	Benz (a) Anthracene Spectra	19
8	Benzo (e) Pyrene Spectra	20
9	Benzo (ghi) Perylene Spectra	21
10	^{14}C BaP Tracer Correction Factor Variation With Sampling Time	29
A1	HPLC Analysis - Sample II-7	34

ABBREVIATIONS

BaA	=	Benz(a)anthracene
^{14}C BaA	=	Radioactive Benz(a)anthracene
BaP	=	Benzo(a)pyrene
^{14}C BaP	=	Radioactive Benzo(a)pyrene
BeP	=	Benzo(e)pyrene
BghiP	=	Benzo(g,h,i)perylene
BHP	=	Brake horsepower
DDAD	=	Detroit Diesel Allison Division
HPLC	=	High Pressure Liquid Chromatography
kPa	=	Kilopascals
N_2	=	Nitrogen Gas
PNA	=	Polynuclear Aromatic Hydrocarbons
ppb	=	Parts per billion
nm	=	Nanometers
UV	=	Ultraviolet
µg	=	Micrograms

I - OBJECTIVE

Initially, our objective was to survey PNA emissions from a number of diesel engines by using sampling and analytical procedures that we had developed during the first year of the project. Unfortunately, we found that emission measurements from the DDAD and Mack engines were not reproducible when we used these procedures. Because of this, the project's supervisory group decided that more procedure development was needed, and they redefined the objective: first, find those sampling and analysis factors that affect reproducibility and accuracy; and second, to improve reproducibility and accuracy.

II - SUMMARY

1. During the second year of this project, we developed improved sampling and analysis methods for PNA in diesel exhaust. To do this, we worked mainly with one engine at a few fixed speeds and loads and usually confined our emission measurements to two PNA species, namely, BaP and BaA. We used the ^{14}C isotopes of BaP and BaA as tracers to compensate for losses in sampling and analysis.

2. We modified the sampling system that we had developed in the first year by diluting the exhaust sample with chilled air (2 to 4 times by volume). We did this in order to keep the exhaust filter at 30°C or lower. These changes helped to reduce PNA losses. We also applied an improved method of injecting radioisotopic PNA tracer into the diluted exhaust sample.

3. We switched from benzene-methanol to benzene as the filter extractant because pure benzene extracts fewer polar compounds. The polar compounds interfere in the subsequent PNA analysis. In addition, we added a high pressure liquid chromatography separation procedure to further purify individual PNA's for quantitative determination by UV spectroscopy.

4. Isotopic dilution with ^{14}C PNA's proved to be very valuable, even essential, in compensating for the PNA sampling and analysis losses. For example, for four runs at one operating condition, the loss-corrected BaP emission rates were 20-27 µg/kg

fuel, whereas the uncompensated rates were only 1.5-6.4. Likewise, for these same four runs, the loss-corrected BaA measurements showed 51-89 µg/kg fuel whereas the uncompensated rates were only 10.3-26.9. At a second operating condition, the loss-corrected BaP emission rates were 4-11 µg/kg fuel while the uncorrected rate was 1.5-3.6 µg/kg fuel. Similarly, the loss-corrected BaA measurements were 17-41 µg/kg fuel whereas the uncorrected rates were 6.6-12.5. We observed similar beneficial results for a third operating condition.

5. While the use of ^{14}C PNA tracer compensated for PNA losses in sample collection and analysis and improved reproducibility of the PNA measurements, it did not reduce the PNA loss. We do not yet know whether these losses occur principally during sample collection or in the analytical procedure.

6. PNA emissions from the Mack ENDT-675 engine were:

	PNA Emissions			
	µg/kg Fuel		µg/m³ Exhaust	
Engine Operation	BaP	BaA	BaP	BaA
No Load, 1260 RPM	25	68	0.4	1.0
1/2 Load, 1260 RPM	8	32	0.3	1.1
Full Load, 1800 RPM	16	16	0.6	0.7

7. PNA losses increased with sampling time. The losses were greatest at full engine load and least at half engine load.

III - RECOMMENDATIONS

We offer two recommendations:

1. Determine which steps or factors of the sampling and analysis procedures are responsible for major losses of PNA. This is important and offers the potential reward of eliminating the requirement to add PNA isotopes to the dilute exhaust for PNA loss accounting. Without the requirement to introduce isotopic tracer into the dilute exhaust, particulate matter could readily be collected for cyclic engine operation using CVS systems.

2. Institute a project to attain the objective originally assigned CAPE-24-72. The assignment would include item 1, above.

IV - INTRODUCTION

At the outset, in the first year of this program, we sampled for PNA from hot undiluted exhaust on Chromosorb 102 absorbent, which has a strong specific affinity for aromatic compounds. The quantity of individual PNA recovered for final measurement in these experiments was so near the limit of measurement of the UV absorption method and the variability of the emission so great that we had little confidence in the results. Subsequent application of radioactive BaP and BaA tracers showed that most of these PNA were destroyed in sampling and/or analyses, leaving too little for accurate measurement. A variety of modifications to this small scale sampling system were tried, still taking undiluted exhaust gas, without significant benefit. Furthermore, we were missing BaA altogether, even though we had reason to expect it.

Therefore, shortly into this second year, we realized that before we could accomplish the objective of the project (determining PNA emissions from several engines at various speeds and loads), we had to develop a more adequate system of sampling and analyses. As a consequence, we revised the sampling system, modified the analytical method for PNA, and limited engine operation to three steady-state conditions.

These developments, and some emission measurements obtained with the revised procedures, are given in the report.

V - EXPERIMENTAL PROCEDURES

A. Engines & Fuels

Two engines were used in this study of PNA emissions: a DDAD 3-53 two cycle engine and a Mack ENDT-675 six cylinder, four cycle, turbocharged direct injection engine. The Mack was installed early in the second year.

The fuel used in all of this year's work was a number 2 diesel fuel made by compositing ten commercial #2 fuels and designated 2-16 in the first year's report. Inspection data are given in Table B2 of Appendix B.

Engine speed, load, fuel flow, air flow and temperatures were measured using conventional instrumentation.

B. PNA Sampling System Development

Exhaust gas was sampled through a 1/2" stainless steel probe that extended across the exhaust pipe two meters from the engine turbocharger. The probe was sealed at the end and had 24 1/16" holes drilled into the quadrant of the tube that faced upstream to the exhaust flow. This probe was used throughout the study. Figure 1 illustrates the exhaust emissions sampling system selected as suitable for use with a proportional sampler and cyclic engine operation. This sampling system was used with undiluted exhaust in experiments D27 through I-8.

Figure 2 shows the system that was adopted after it was decided that we would operate at steady speed and would cool and dilute the exhaust samples. Dried air is chilled, by passing through a coil immersed in a bath of dry ice and methanol, to a temperature that gives a diluted sample temperature of between 20 and 30C; the degree of cooling required depends on the dilution ratio and the initial temperature of the exhaust gas. The dilution ratio is the ratio of dilution air to exhaust gases in the sample. It is calculated as follows:

$$\text{dilution ratio} = \frac{[x]_r}{[x]_d} - 1,$$

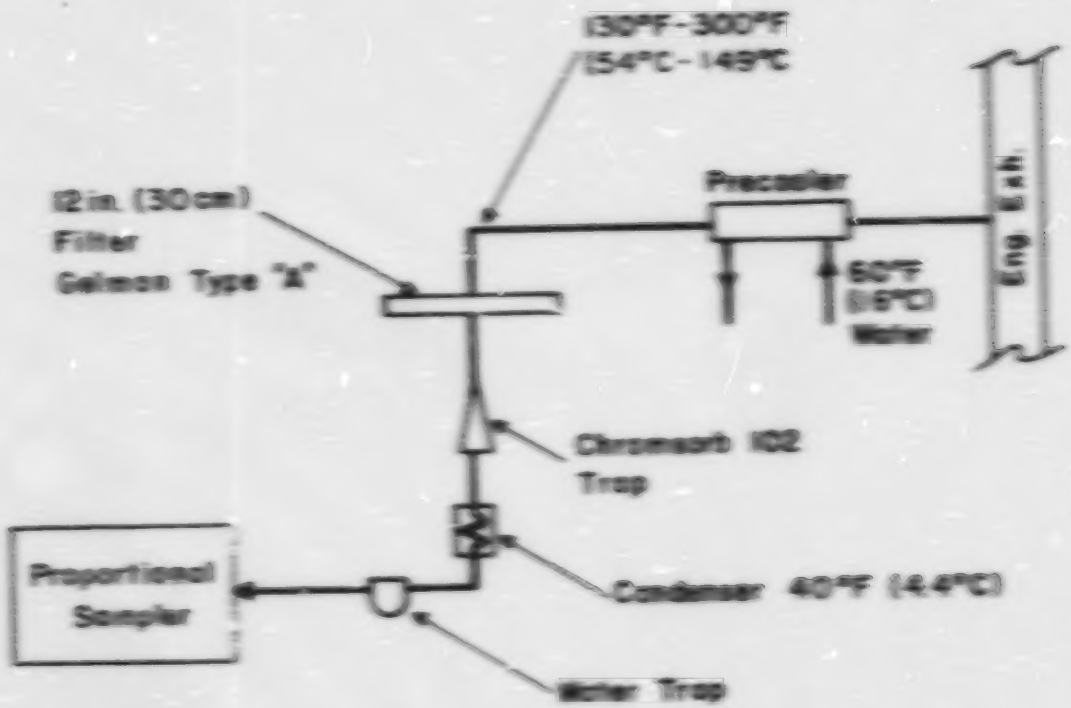
where $[x]_r$ is the concentration of either CO_2 or NO_x in the raw exhaust and $[x]_d$ is the concentration of the same component in the diluted sample. Dilution ratios of 3 to 1 were maintained at a mixture temperature of 20 to 30C. Attempts to hold a dilution ratio of 2 to 1 at 20C caused ice to form which restricted the flow of exhaust gases. Therefore, we generally avoided dilution ratios below 3. This sampling system was used in experiments I-9 through I-13.

Figure 3 shows the latest modifications made to the sampling system in which the tracer flow from the reservoir was controlled by N_2 pressure rather than by a motor-driven syringe. Heat control to the nitrogen carrier gas was also modified as shown in detail in Figure 4. A large pump was installed to increase

FISURE I

PNA COLLECTION SYSTEM (I) IN USE

AT END OF FIRST YEAR



BIBLIOGRAPHIC DATA SHEET	1. Report No. CRC-APRAC-CAPE-24-72	2.	3. Recipient's Accession No.
4. Title and Subtitle: Polynuclear Aromatic Content of Heavy Duty Diesel Engine Exhaust Gases - Second Year Report			5. Report Date: January 17, 1977 6.
7. Author(s): R. S. Spindt			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: Gulf Research & Development Company P. O. Drawer 2038 Pittsburgh, Pennsylvania 15230			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address: Coordinating Research Council, Inc., 30 Rockefeller Plaza New York, N.Y. 10020; and Environmental Protection Agency, Research Triangle Park, N. C. 27711			13. Type of Report & Period Covered: Second Year 14.

15. Supplementary Notes

16. Abstracts: During the second year of this project, we developed improved sampling and analysis methods for PNA in diesel exhaust. To do this, we worked mainly with one engine at a few fixed speeds and loads and usually confined our emission measurements to two PNA species, namely, BaP and BaA. We used the ^{14}C isotopes of BaP and BaA as tracers to compensate for losses in sampling and analysis. We modified the sampling system that we had developed in the first year by diluting the exhaust sample with chilled air (2 to 4 times by volume). We switched from benzene-methanol to benzene as the filter extractant because pure benzene extracts fewer polar compounds. Isotopic dilution with ^{14}C PNA's proved to be very valuable, even essential, in compensating for the PNA sampling and analysis losses. While the use of ^{14}C PNA tracer compensated for PNA losses in sample collection and analysis and improved reproducibility of the PNA measurements, it did not reduce the PNA loss. We do not yet know whether these losses occur principally during sample collection or in analytical procedure.

17. Key Words and Document Analysis. 17a. Descriptors

Air Pollution
Exhaust
Emissions
Diesel Engine
Gasoline Engine
Polynuclear Aromatics
Hydrocarbons

17b. Identifiers/Open-Ended Terms

17c. COSATI Field Group: 07C; 13B; 21B; 21G; 21D.

18. Availability Statement: Releasable to the general public.	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 50
	20. Security Class (This Page) UNCLASSIFIED	22. Price PC N02, A01

FORM NTIS-35 (REV. 10-73) ENDORSED BY ANSI AND UNESCO. THIS FORM MAY BE REPRODUCED USCOMM-DC 8265-P74

FIGURE 2
PNA COLLECTION SYSTEM (2)
WITH TRACER INJECTION AND
AIR DILUTION ADDED

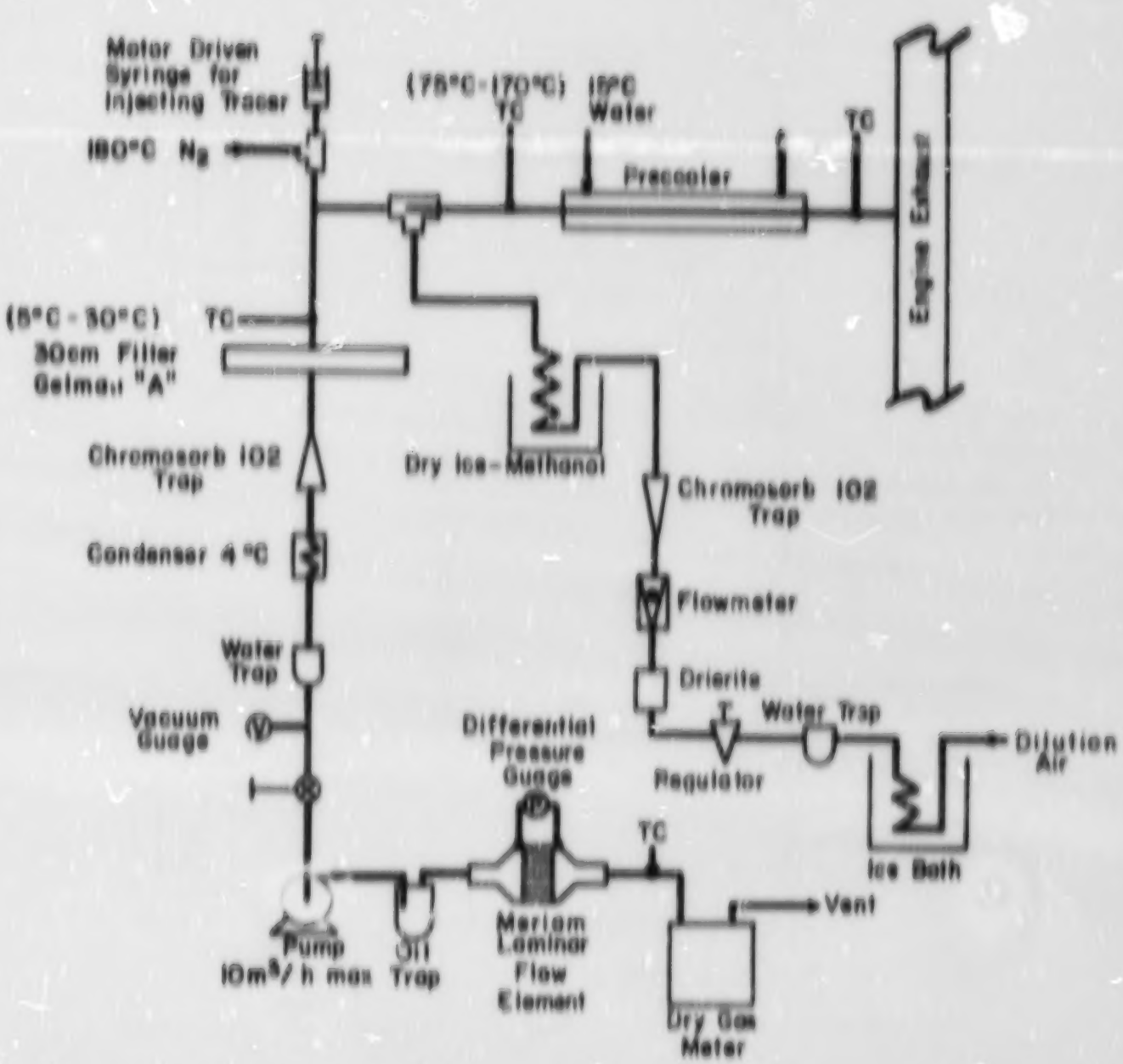


FIGURE 3

PNA COLLECTION SYSTEM (3)
WITH MODIFIED TRACER INJECTOR

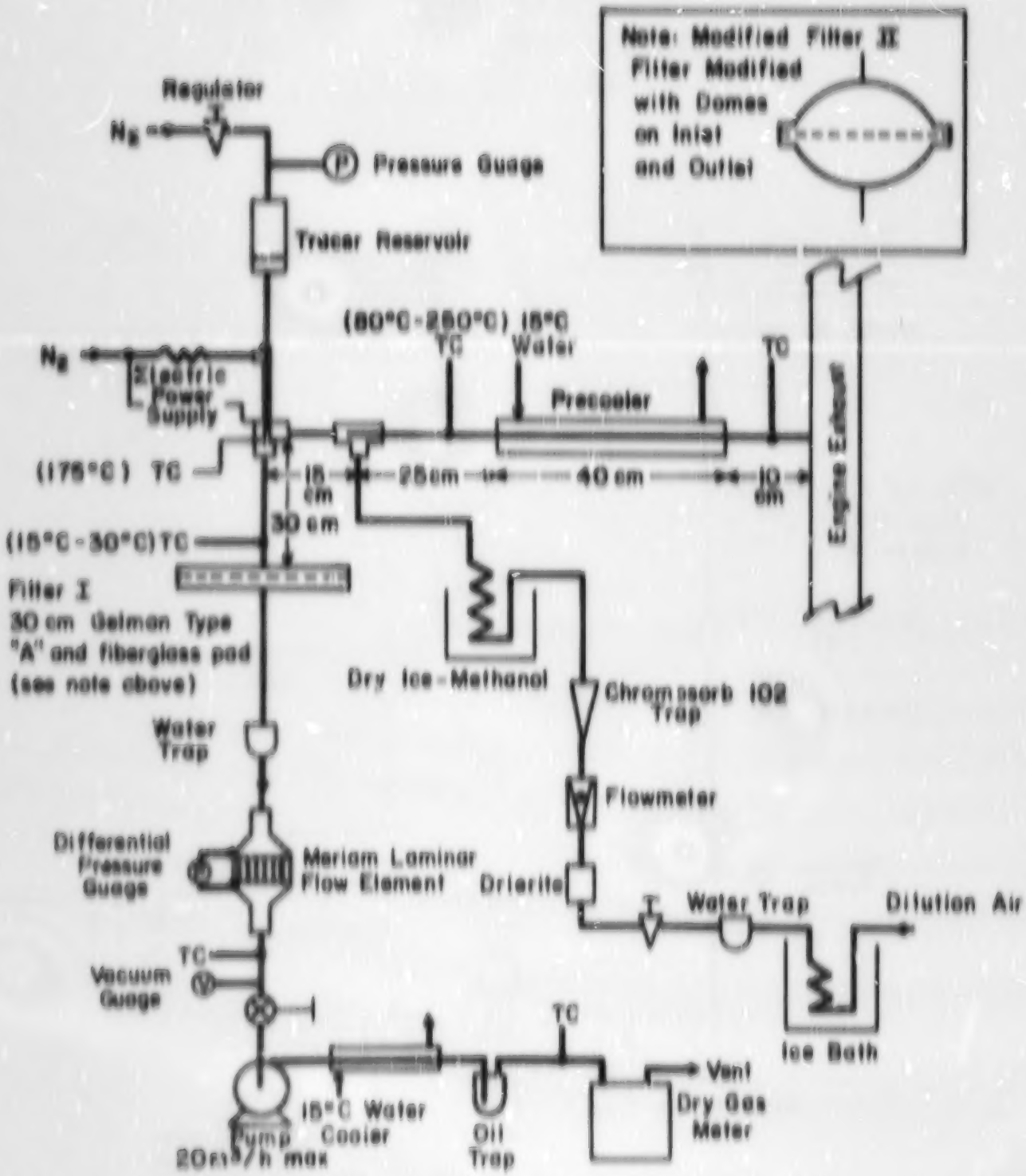
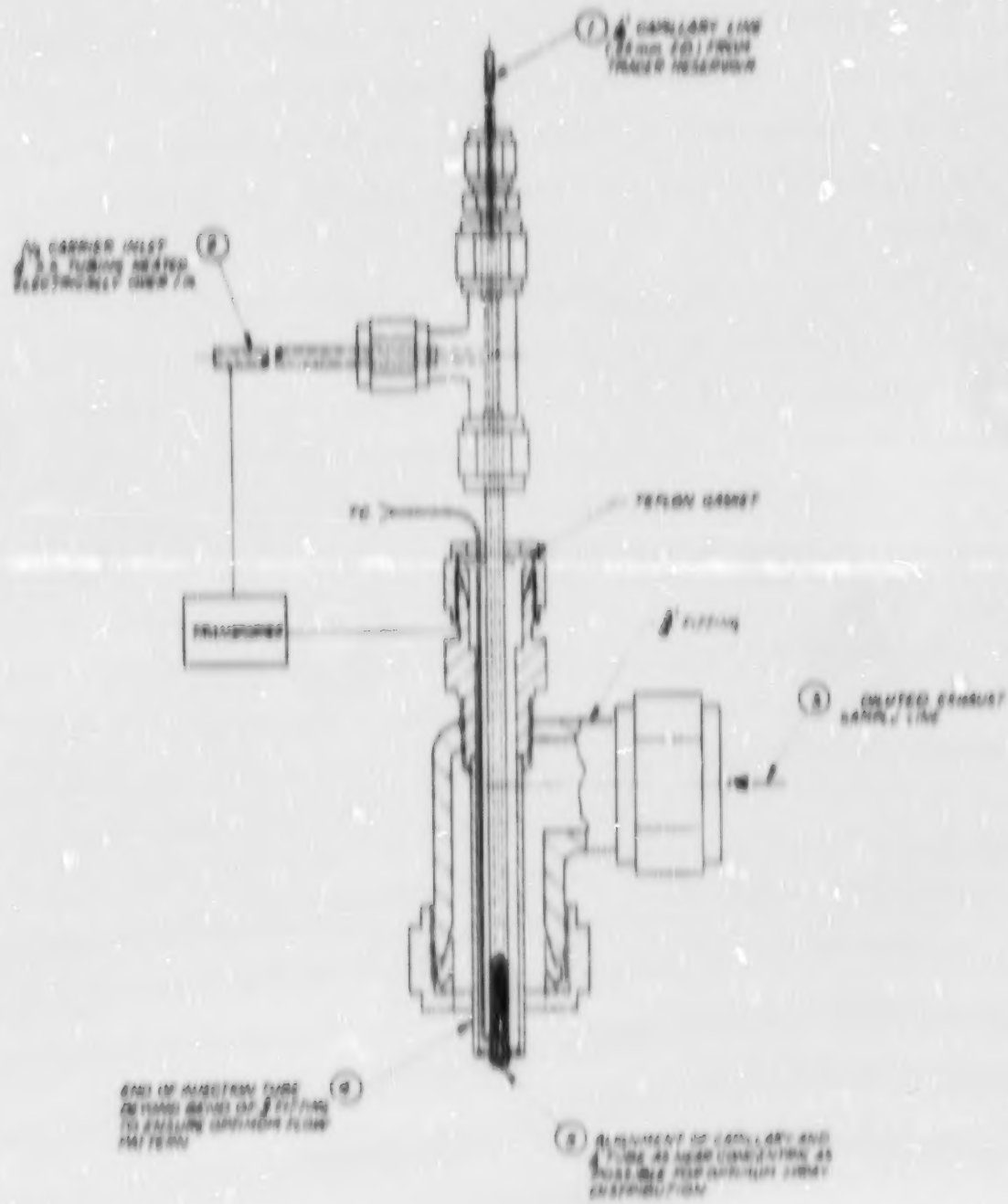


FIGURE 4

ISOTOPIC TRACER INJECTION SYSTEM



the sampling rate.

Flow of the tracer in isooctane solution through the hot part of the injection system is limited by the viscosity of the isooctane vapor in the capillary tubing. Since leakage around the barrel of the motor-driven syringe is possible if too fast a flow were attempted, the change to N_2 pressure flow control eliminated this problem.

Particulate matter was filtered from the system using a 30 cm diameter Gelman type A glass fiber filter. These filters were initially cleaned of soluble organics by heating overnight in air at 260C. For experiments II-1 through II-10, an experimental PPG fiberglass pad was placed ahead of the glass filter to collect the bulk of the larger soot particles. This pad was also given a pretreatment overnight in a furnace at 360C to remove organic material.

Starting in experiment II-13, the filter housing was changed from a narrow wedge-shaped liquid filter to a larger volume balloon-shaped filter. This was accomplished by cutting out the center portions of the housing and welding on stainless steel bowls with new inlet and outlet fittings. This alteration did not improve the filtering capability, but it did improve the uniformity of the particulate distribution on the filter.

For the sampling system shown in Figure 1, sample volume was measured and controlled by a variable rate proportional sampler. For the steady-state air-diluted sampling systems of Figures 2 and 3, sample flow was measured using a dry gas test meter. Initial flow rates were set using the Meriam air flow instrument and the vacuum gauge.

C. Distribution of Tracer in Sampling System

Before the apparatus shown in Figure 4 was used with an engine sample, four bench experiments were conducted to determine where the tracer would collect in the system. In these experiments, non-radioactive BaA and BaP were injected into an air stream at temperatures and flow rates comparable to normal sampling

conditions. In this case, the system was clean, i.e., no soot was present. Figure 5 shows the various sampling positions from which the PNA was recovered. The results are reported in Table I.

The data show that the PdA, added as a hot vapor in isooctane and nitrogen (184C) but cooled to 25C in the air stream, collects at various locations in the system in a non-uniform manner. This finding indicates the need to clean all parts of the sampling system well to ensure recovering all of the tracers when they are added to an exhaust sample. However, total recovery of BaP and BaA was good and independent of the amount introduced. That is, it was equally accurate to measure 2 ug distributed in various locations as it was to measure 20 ug.

The fact that no PNA were found on the Chromosorb 102 trap confirmed that BaP and BaA, when cooled to room temperature, condensed and deposited on the surfaces of the lines and filters. As a result of these experiments, we stopped using a Chromosorb trap with chilled exhaust samples starting with Experiment II-1.

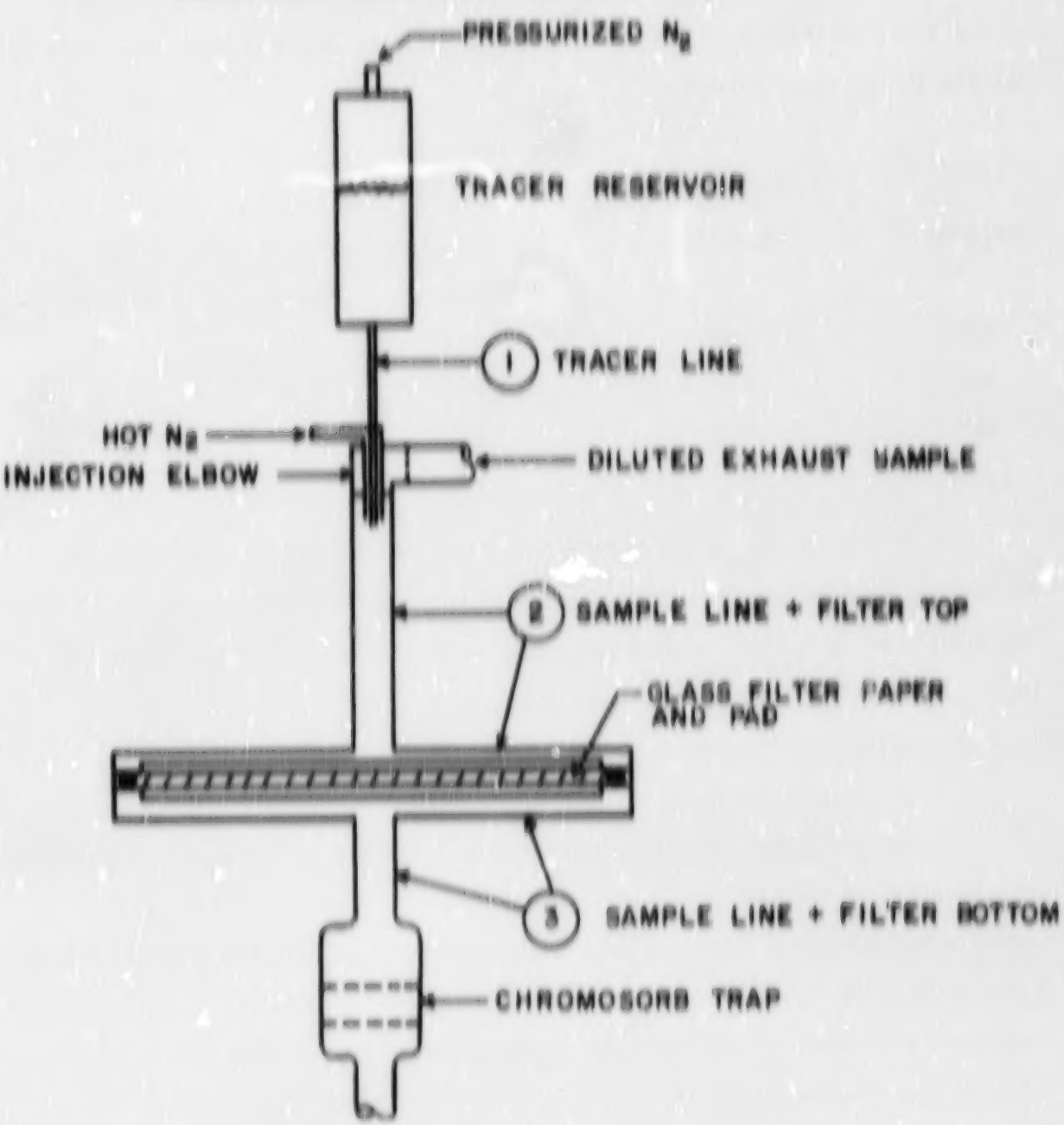
B. Solvent Selection for PNA Extraction From Soot

The complexity of diesel exhaust is known to be great. In addition to complex hydrocarbons collected with the soot, there are numerous partial oxidation products, including phenols, acids and possibly peroxides. The analytical procedure used to separate the PNA must quantitatively isolate those compounds of interest to the exclusion of all other compounds that will interfere. Solvent choice will affect the amount of extraneous material taken into the sample as well as efficiency of recovery of the PNA as indicated in Table II. Clearly, a solvent that is efficient for PNA but not for extraneous material is desirable.

Three experiments were performed to evaluate the solvent used to extract the PNA from the soot. Table II gives the results of this study which used quarter pieces of filter coated with an engine soot and which had not been previously extracted. The recovered PNA represents not only the synthetic PNA added but the

| | | |

FIGURE 5
SYSTEM SAMPLING LOCATIONS



material originally on the filter. Clearly, when less PNA was recovered than was added, either the solvent is less efficient or there has been extensive reaction. Since benzene gives the highest total recovery of those solvents used, it is the preferred solvent. The higher percent recovery of PNA compounds is likely due to the lower solubility of the reactive polar material material which had degraded the PNA in the other solvents.

TABLE II

EFFECT OF SOLVENT ON PNA RECOVERY FROM SOOT

Compound	ug Added	Total ug Recovered With Solvent		
		Benzene	40-60 Methanol-Benzene	Dichloro Methane
BaP	1.03	.89	.60	.84
BaA	1.06	1.80	1.85	1.41
BeP	0.94	.89	.61	.69
BghiP	1.07	1.00	.16	.39

At the outset, we measured phenols in addition to PNA. The more polar benzene-methanol solvent was preferred for the more polar phenolic compounds. When the project group decided to drop the phenol analysis, benzene alone became the preferred solvent.

B. Analytical Procedures for PNA

1. Separation Steps

The analytical procedure described in the first annual report, consisting of separation on two alumina columns, thin layer separation on cellulose fiber coated glass plates and finally, thin layer separation on cellulose acetate coated glass plates, was found to work well with fuel samples but not for diesel soot samples. As a result, a new step, HPLC, chromatography, was added to the scheme after initial separation on the cellulose plate. This added purification step did isolate BaA. The complete analytical separation scheme is described in Appendix A.

The experiments listed in Table III demonstrate that this separation scheme works. Synthetic (non-radioactive) mixtures of four PNA were separated under several conditions. The weight of the four compounds in the table were obtained by taking aliquots of each PNA compound in benzene solution to give a mixture with the indicated weight in one ml of solution.

TABLE III

ANALYTICAL RECOVERY VALIDATION OF FOUR PNA BLENDED IN BENZENE

Compound	(µg Added)	Percent Recovery Experiment				
		HPLC Only		Complete Procedure		
		1	2	3	4	5
BaP	0.98	85	84	73	67	79
BaA	1.11	78	85	87	75	96
BeP	0.94	68	72	76	64	72
BghiP	0.90	86	91	85	72	74

In Experiments 1 and 2, the reference mixture was separated, after concentration of the benzene solution, by the HPLC procedure alone. The individually recovered fractions were measured in 1 ml of hexadecane by UV absorption. In Experiments 3 and 4, the reference mixture was put through the complete separation process starting with the initial separation on the alumina columns. Experiment 5 was like Experiments 3 and 4, except that recovered background material* from a previous engine run was added to the reference mixture.

Two additional experiments were conducted with added background material. In one, the reference sample of PNA plus a ^{14}C BaP spike was placed on the extracted soot from a previous engine run. The recovered background material from this run was placed in a still pot with 200 ml of benzene-methanol azeotrope and used to

* The background material comprised all of the material extracted from the soot that could be recovered from the separation steps by solvent extraction from the alumina column, the TLC plates and the HPLC column.

extract the soot in a Soxhlet thimble. The recovery of PNA after 13 hours of extraction was as follows:

BaP	39%
^{14}C BaP	77%
BaA	98%
BeP	35%
BghiP	15%

This experiment demonstrated that during extraction and analysis, some PNA are lost.

In the second experiment, the background material was recovered again and heated at reflux with the reference PNA mixture (without ^{14}C BaP) for 16 hours (no Soxhlet apparatus or soot). The following recovery was obtained:

BaP	57%
BaA	99%
BeP	60%
BghiP	84%

This experiment demonstrated an improved recovery possibly as a result of deactivation of the recovered tars.

These experiments suggest that the background material, even after recovery from the separation process, contains compounds that will chemically react with some PNA when heated for a period of time. Specifically, the low recovery of BaP, BeP, and BghiP is well below what would be expected from manipulating the sample (Table III) and probably represents chemical degradation. Since these experiments used a recovered background material, it is possible that this material had been altered during the several separations to be less active.

Our experiments with the extracted tars emphasizes the need to account for losses during sample extraction and component separation.

2. <u>UV Spectrophotometry</u>

The choices of solvent and analytical procedure are designed to provide

recovered PNA compounds of sufficient purity that they can be measured accurately by ultraviolet spectrophotometry. Non-PNA compounds in diesel exhaust have a generalized background absorption in this same region, increasing with decreasing wavelength. This impurity is compensated by using the slant baseline technique of measurement, figures 6 through 9. The amount of such impurities has been reduced sufficiently to avoid interferring significantly with PNA estimation when using the slant baseline technique.

The analytical instrumentation used for measuring individual PNA is a Cary 17 Ultra Violet Spectrophotometer. Based on our calibrations with this instrument, 0.1 µg BaP is equivalent to approximately one scale division (2 mm) at an attenuation of one. This measurement is interpolated to .5 mm. Therefore, measurements of peak height yields a sensitivity of ±0.001 µg BaP.

Measurments of radioactive tracers is done by counting disintegrations of carbon 14 in the recovered PNA (BaP or BaA). Usually, counting is continued until at least 10,000 counts above background are obtained which gives a counting accuracy of about one percent. Overall accuracy includes recovery efficiency as well as measurement accuracy.

Experiment I-1 demonstrates the reproducibility of the analytical procedure. This experiment was a 13-mode cycle engine run where the ^{14}C BaP tracer was added to the extract. The sample was divided into two equal parts. One part was analysed immediately, while the other was analysed four days later.

Tracer recovery (Table IV) and engine produced BaP were greater for immediate analysis than for the delayed analysis. However, the corrected recoveries (0.143 and 0.160 µg) agree to better than 0.02 µg. In this experiment, there was not much degradation in the sample stored 4 days in a refrigerator. This suggests that samples can be obtained in the field, extracted, and the extract taken in a cold container to a central laboratory for analysis. While differences of 0.02 µg represent good repeatability, the absolute level of PNA at 0.15 µg are

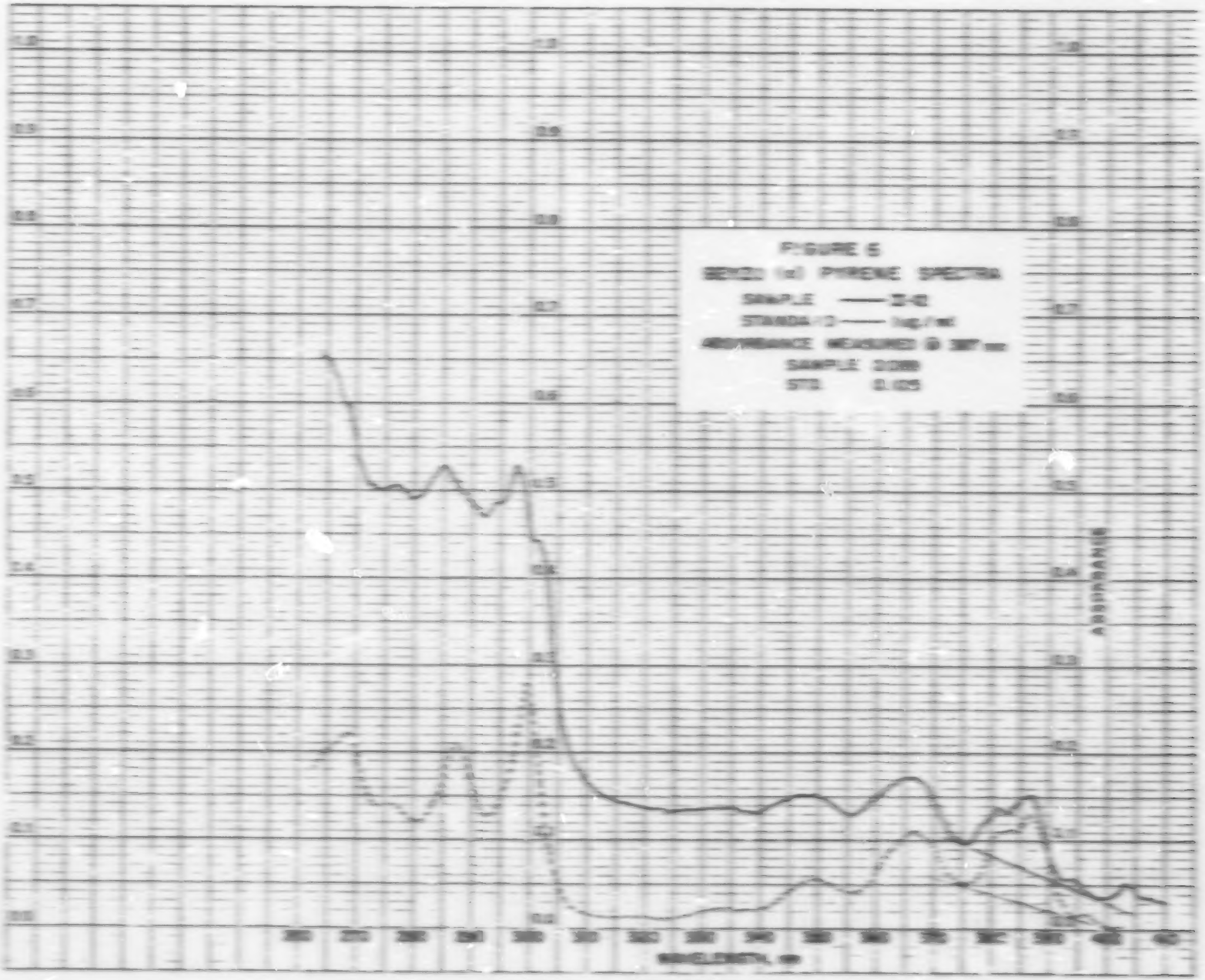


FIGURE 6
SAMPLE
SAMPLE 2088
570 0.025

FIGURE 7
INFRARED SPECTRA OF ANTHRACENE
SAMPLE — 21-C
STANDARD — NBS
SAMPLE KBr DISC
REFERENCE — KBr DISC

FIGURE 8
BENZO (a) PYRENE SPECTRA
ABSORBANCE
WAVELENGTH

ABSORBANCE
WAVENUMBER (cm⁻¹)
FIGURE 9
INFRARED SPECTRA
OF CONDENSED POLYCYCLIC AROMATICS
FROM STACK SAMPLE
SAMPLE
H-2
STANDARD
ACID

too low to be considered acceptable. Results of this magnitude caused us to undertake the improvements in sampling and analysis procedures just described.

TABLE IV

REPRODUCIBILITY OF DIVIDED SAMPLE ANALYSES

Sample	I-1 Initial	I-1 4 Days Later
Tracer Added, µg	.11	.11
Tracer Recovered, µg	.046	.030
Correction Factor	2.39	3.70
Total Measured (uv), µg	.076	.051
Engine Produced, µg	.030	.021
Corrected Yield, µg (Based on Total Sample)	.143	.160

VI - RESULTS AND DISCUSSION

A. Evidence for the Need to Redirect the Study Objective

The initial effort for this second year's program was to evaluate the emissions from the two engines used in this project employing cyclic test procedures. Data for the DDAD and Mack Engine were obtained using both the 13 mode and smoke cycles and the sampling system of Figure 1 involving sampling raw exhaust gases.

Four smoke cycle experiments (D278D-30) were made with the DDAD engine. The absolute amount of BaP found from the engine in these experiments, from which about $7m^3$ of exhaust gases was sampled, varied from 0.03 to 0.44 µg, close to the limit of UV detection. In only one run was any BaA found although it was regularly found after modifying the separation procedure. While ^{14}C BaP was used as a tracer in these runs, it was added to the solvent after extraction of the soot. Because of this fact, there is no estimate of sampling or extraction losses which often have been found to be significant. The yield of BaP corrected for analytical losses varied from 0.40 to 4.3 µg/kg fuel burned, much less than was expected

and later found for steady state conditions.

Three smoke cycle experiments (I-3, I-4 and I-8) were made using the Mack engine. Again the absolute recovery of BaP varied from 0.01 to 0.09 ug with a tracer correction factor varying from 2.4 to 364 which gave corrected yields from 0.23 to 17 ug/kg fuel.

Five 13 Mode cycle experiments (I-1, I-2, I-5, I-7 and I-12) were run in the Mack engine. Sampling was done on an equal time weighted basis rather than on an individual mode analysis. The absolute recovery of BaP ranged from 0.10 to 0.14 ug. When tracer was added to the extract, the tracer recovery amounted to 20 and 35 percent; when it was added to the filter prior to extraction, the tracer recovery was 1.4%, while when it was added during exhaust gas sampling, the recovery was 5.3 and 1.9%. The corrected recovery of BaP ranged from .23 or .34 ug/kg when the tracer was added after extraction, to 23 ug/kg when it was added to the filter, and to 5.3 to 22 ug/kg when it was added to the exhaust.

The results of these three sets of experiments showed (1) that we were not obtaining enough sample to be confident of the analytical results, (2) that we had a high variability in the data and (3) that there appeared to be excessive losses during either sampling or extraction that would not be accounted for by adding tracer to the extract. As a result, we concluded that it was necessary to take steps to validate our procedures.

For these reasons, we added the HPLC step to the analytical procedure, shortened the extraction times, switched to benzene alone as the extractant, and arranged to sample at a higher rate with exhaust gas diluted with chilled air.

B. PNA Emissions at No Load Operation

Table V summarizes four engine experiments at no load operation. In each of these runs, tracer was injected into the cooled dilute exhaust sample. Sampling time and dilution ratio were varied as indicated. BaP tracer recovery varied from 6 to 24%. The best tracer recovery was obtained at the shortest

sampling time.

In spite of the variation in loss of tracer, the corrected yields of BaP averaged 25 μg/kg fuel with only 13% coefficient of variation. Similarly, BaA averaged 68 μg/kg fuel with 37% coefficient of variation. Since tracer was added during sampling whatever the source of loss, the corrections for this loss give reasonably constant final data.

TABLE V

EFFECT OF SAMPLING TIME AND DILUTION RATIO ON PNA

EMISSIONS AT NO LOAD, 1260 RPM

IN MACK ENGINE

Run	11-8	11-9	11-10	11-11	Average
Load (water drag) hp	14	14	14	14	-
Sampling Time, hr	2	2	1	0.5	-
Sample Volume, m^3	10.8	10.6	5.2	4.0	-
Dilution Ratio	3	3	3	1.3	-
Tracer Corr. Factor: BaP	10.8	17.8	5.3	4.1	-
BaA	4.3	5.3	3.3	4.1	-
Measured from Engine, μg: BaP	.28	.22	.38	.36	-
BaA	1.79	1.49	1.97	1.10	-
Corrected Yield, $\mu g/m^3$: BaP	0.29	.37	.40	.37	.36
BaA	0.71	.75	1.25	1.13	.96
μg/kg Fuel: BaP	20	27	27	27	25
BaA	51	54	89	80	68

C. PNA Emissions at Half Load Operation

Table VI summarizes five engine experiments at half load operation. Four of these runs were made using sampling system 2 and, in three, methanol-benzene rather than benzene was used as the extractant. The ^{14}C BaP recovery varied from

19 to 34% with one of only 1.3%. This last result occurred at low dilution and long sampling time. Since the tracer recovery was so low in this run, we can place no confidence in the BaP result and the data have been excluded from the average. This was not true of the BaA which is apparently more stable.

These data suggest that shorter sampling time and increased dilution are both beneficial in stabilizing the BaP in the sample.

TABLE VI

EFFECT OF SAMPLING TIME AND DILUTION RATIO ON PNA EMISSIONS AT HALF LOAD, 1260 RPM IN MACK ENGINE

Run	I-9	I-10	I-11	I-13	II-12	Average
Load, HP	90	90	90	90	93	-
Sampling Time, hr	3.6	3.1	3.3	11.6	1	-
Sample Volume, m^3	5.5	5.2	5.3	48.6	5.3	-
Dilution Ratio	4	4	4	1.4	7	-
Tracer Correction Factor:						
BaP	5.2	2.9	3.2	77	4.2	-
BaA	2.9	1.4	3.8	5.2	4.6	-
Measured From Engine, µg:						
BaP	.43	.34	.27	1.84	.43	-
BaA	2.21	2.36	2.13	13.5	1.09	-
Corrected Yield, $\mu g/m^3$:						
BaP	.41	.19	.16	2.92*	.34	.28
BaA	1.16	.62	1.34	1.44	.94	1.1
Yield, µg/kg fuel:						
BaP	11	5	4	79*	11	8
BaA	32	17	41	39	30	32

* Excluded from average.

D. PNA Emissions at Full Load Operation

Table VII summarizes six engine experiments at full load operation. Four of these experiments were conducted with tracer (in isooctane) injected into the cooled, dilute exhaust sample and all show large loss of BaP. The BaP data for II-2 have been excluded from the average of these four experiments because of the tracer correction factor which is too large to be confident of the results.

Experiment II-15 is like II-13 and II-14 except that tracer was not added during sampling but to the filter before extraction. The tracer correction factor is much smaller (better recovery) and the amount of PNA measured from the engine is larger. When the correction is applied to the measured values, the corrected yields in $\mu g/m^3$ or $\mu g/kg$ fuel approaches the average from the first four runs. These experiments suggest that injection of the tracer has seriously affected the recovery of PNA from the sample.

Experiment II-16 supports this suggestion. In this run, the tracer was added to the filter before extraction while isooctane alone was injected into the sample gases. The tracer recovery in II-16 was equal to that of II-15 and much better than in II-13 or II-14. On the other hand, the amount measured from the engine is low, equal to that found in II-13 and II-14 compared to the amount found in II-15. We conclude that the addition of isooctane to the sample gases resulted in some reactions that cause a loss in PNA, particularly BaP. Whether the actual losses occurred during sampling or at a later step is not defined by these data. What was done during sampling could have affected the extraction or separation later. Since funds are unavailable for further work, we have not been able to further confirm this observation.

These results do show that losses are affected by sampling procedures and that there are losses during extraction and analysis which must be compensated for by use of radioactive tracers.

TABLE VII

EFFECTS OF SAMPLING TIME AND SAMPLE TREATMENT ON PNA EMISSIONS AT FULL LOAD, 1800 RPM IN MACK ENGINE

RUN	II-1	II-2	II-13	II-14	Avg.	II-15	II-16
Treatment	a	a	a	a		b	c
Load, HP	211	205	202	202		204	205
Sampling Time, hr	1.9	4.0	1.0	1.0		1.0	1.0
Sample Volume, m^3	10.0	14.9	5.0	5.0		4.9	4.9
Dilution Ratio	3	3	3.1	3.0		3.1	3.1
Tracer Correction Factor:							
BaP	56	400	32	28		3.1	2.1
BaA	28	60	9.5	8.6		1.8	3.3
Measured from Engine:							
BaP, µg	.10	.16	.10	.13	.12	1.32	.14
BaA, µg	.06	.24	.48	.41	.30	1.85	.36
Yield, $\mu g/m^3$							
BaP	.56	[illegible]	.65	.69	.63	.84	.058
BaA	.17	.94	.90	.73	.68	.60	.34
Yield, µg/kg Fuel							
BaP	14	100*	16	17	16	20	1
BaA	4	23	23	17	16	14	6

a Tracer injected into exhaust sample stream.

b Tracer added to filter in soxhlet thimble after sample collection, injection.

c Tracer added to filter in soxhlet thimble after sample collection but isooctane vapor added to sample through normal injection process.

* Excluded from average because of excessive correction factor.

E. Effect of Sampling Time & Dilution on PNA Losses

Figure 10 illustrates how the ^{14}C BaP correction factor varies with sampling time when tracer is injected into the exhaust sample. Solid symbols represent dilution ratios less than three. The point marked 000 is too poorly measured to be defined accurately since it represents less than 2% recovery.

Tracer recovery appears to be best at the half load condition. Even here, when the dilution ratio is 2, there is an apparent loss of tracer relative to higher dilution ratios.

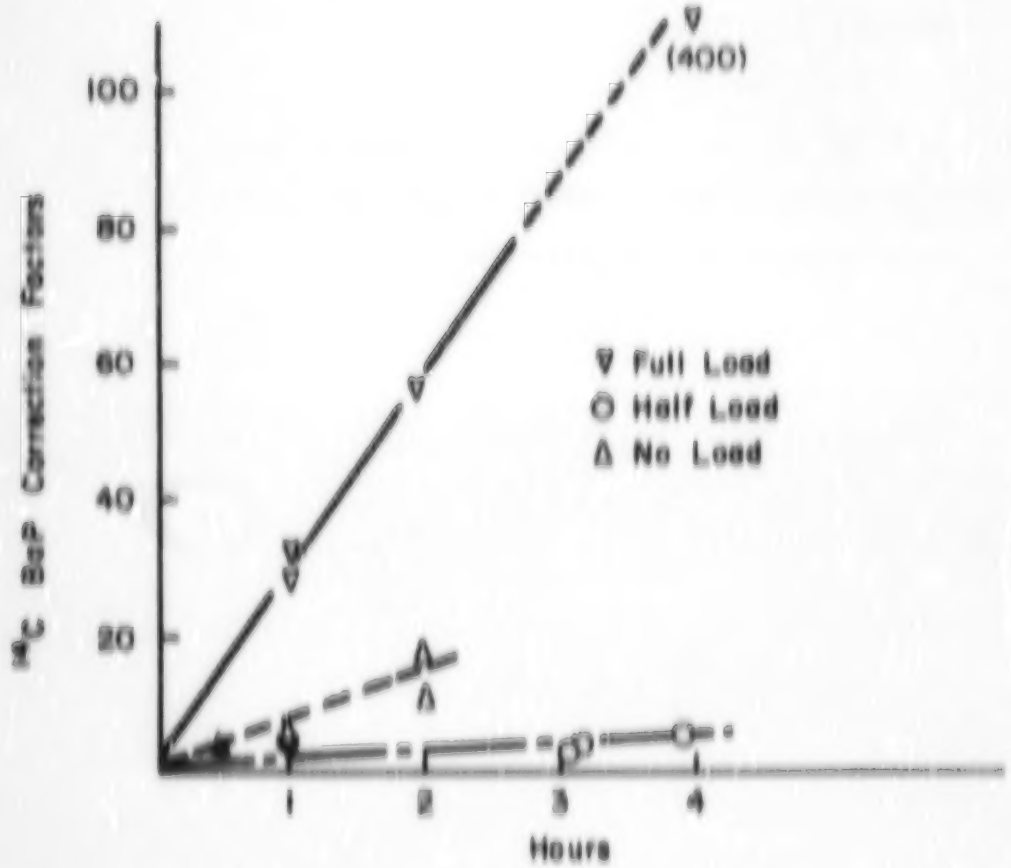
Full load operation results in the highest correction factors (most loss of BaP). No load operation is intermediate. Why no load and full load operation lead to greater destruction of BaP is not clear, but it must be related to the combustion products formed at these conditions.

The correction factor for PNA losses appears to vary linearly with time of sampling. Since the correction is the inverse of the fraction recovered, plotting either the percent recovery or percent loss results in parabolic curves that do not have sufficient points to define unequivocally.

The observation that the correction factor varies linearly with time strongly suggests that there are significant sampling losses that must be corrected for through the use of a tracer. Since these losses appear to be influenced by the isooctane solvent (compare II-15 and II-16 with II-13 and II-14), it is possible that another tracer solvent would minimize this effect.

FIGURE 10

^{14}C BaP TRACER CORRECTION FACTOR VARIATION WITH SAMPLING TIME



REFERENCES

1 Bimonthly report #11 (May 10, 1976) to EPA on Contract No. 68-03-2116 from SwRI.

2 C. M. Begeman and J. M. Colucci, "Polynuclear Aromatic Hydrocarbons from Automotive Engines", SAE Paper 700469, May 1970.

3 L. R. Rechner, W. E. Scott and W. F. Miller, "The Composition and Odor of Diesel Exhaust", Api Division of Refining Jr. Vol. #5 [III] (1965).

PERSONNEL

Supervisory Project Group

Mr. Roger Bascom, Chairman	=	Cummins Engine Company
Mr. E. G. Barry	=	Mobil Research & Development Corporation
Mr. C. R. Begeman	=	General Motors Research Laboratories
Dr. J. F. Coburn	=	Exxon Research & Engineering Company
Mr. D. S. Gray	=	Amoco Oil Company
Dr. Margaret Griffing	=	Ethyl Corporation
Mr. R. J. Hames	=	Detroit Diesel Allison Division, General Motors Corporation
Mr. Gordon Kennedy	=	Environmental Protection Agency
Mr. H. D. Malbin	=	Shell Development Company
Dr. J. M. Perez	=	Caterpillar Tractor Company

Gulf Research & Development Company Personnel

Dr. R. S. Spindt	=	Project Manager
Mr. J. G. Barry, Jr.	=	Project Engineer
Mr. R. A. Brickleyer	=	Project Engineer
Mr. R. S. Dorinsky	=	Technician
Mr. E. D. Hill	=	Research Chemist
Mr. H. S. Norris	=	Senior Research Chemist

APPENDIX A

ANALYTICAL PROCEDURE FOR PNA HYDROCARBONS IN DIESEL EXHAUST GASES

Sample Handling

The exhaust sampling system from the point of tracer addition is disassembled and cleaned thoroughly with a brush using benzene. The filter housing is cleaned the same way and the solvent added to that obtained when the lines were washed. Under subdued light, the solution is filtered through filter paper to collect the solid carbon particles. The benzene washings are stored in a flask under nitrogen in a refrigerator while the particulates are extracted.

The glass fiber and paper filter disks from the collection trap are cut into about 1 cm squares and placed in an extraction thimble along with the filter paper from filtering the line washings.

PNA Extraction

The materials are extracted for two hours with 300 ml of benzene free of PNA. The benzene extract is combined with the line washings while an additional 200 ml of fresh benzene is added and extraction continued for an additional three hours. Usually these last three hours were after working hours and the power to the heating mantle was shut off by an electric timer. The following morning the benzene was combined with the earlier benzene extract and line washings which were stored overnight in the refrigerator.

PNA Concentration

The benzene solution is evaporated on a steam bath to about 10-15 ml. Three ml portions of isooctane are added and each evaporated to 10 ml to provide an isooctane solution in preparation for column chromatography clean up. The hydrocarbon concentrate is placed on a 20 x 1.7 cm glass column containing 15 grams of alumina, Woelm neutral, deactivated with 10% water and eluted with 150 ml of isooctane. The isooctane eluate is allowed to flow directly onto a second

column of the same dimension, but containing 15 grams of alumina, Woelm neutral, deactivated with 2.5% water. After the top column is dry and the bottom column still has a layer of isooctane over the alumina, the bottom column is separated and eluted with 150 ml of benzene. This fraction, which contains the PNA of interest, is concentrated to about 100 µl in benzene and separated on 1 mm cellulose plates using isooctane as the mobile phase.

This procedure was described in the First Annual Report in the fuel oil analysis section. In some instances, when the color level is high, two cellulose plates are used to avoid overloading a plate. The areas containing the PNA of interest are removed from the cellulose plate and extracted with boiling methanol.

High Performance Liquid Chromatography

The PNA concentrate is evaporated to 50 µl in ethanol from methanol by repeated additions of ethanol in a marked conical tube. It is then transferred to a 6 ft. HPLC column containing Bondapak C_{18}/corasil. The PNA are chromatographed starting with 145 ml of a 40/60 water-methanol solution at the flow rate of 2 ml per minute. At 15 minutes into the run, a 25/75 tetrahydrofuran-methanol solution is blended into the water-methanol mixture at the rate of 1 ml per minute. Total elution time is approximately 75 minutes. The effluent from the HPLC was monitored at 254 nm by a Varicean variable wavelength detector equipped with an 8 µl micro cell. The peaks are collected in 10 ml of cyclohexane in a 100 ml volumetric flask. The collection flasks are stoppered, shaken for one minute and diluted into the neck by distilled water. The cyclohexane layer is removed with a pipette. The aqueous layer is extracted with three additional 3 ml volumes of cyclohexane. Figure A-1 illustrates the separation of a typical sample using this procedure. Elution times for PNA of interest are determined by calibration with pure compounds.

Cellulose Acetate Separation

The cyclohexane extracts for each peak are combined, concentrated to about 50 µl and then applied to a 20 x 10 cm cellulose acetate plate, 1 mm thick and

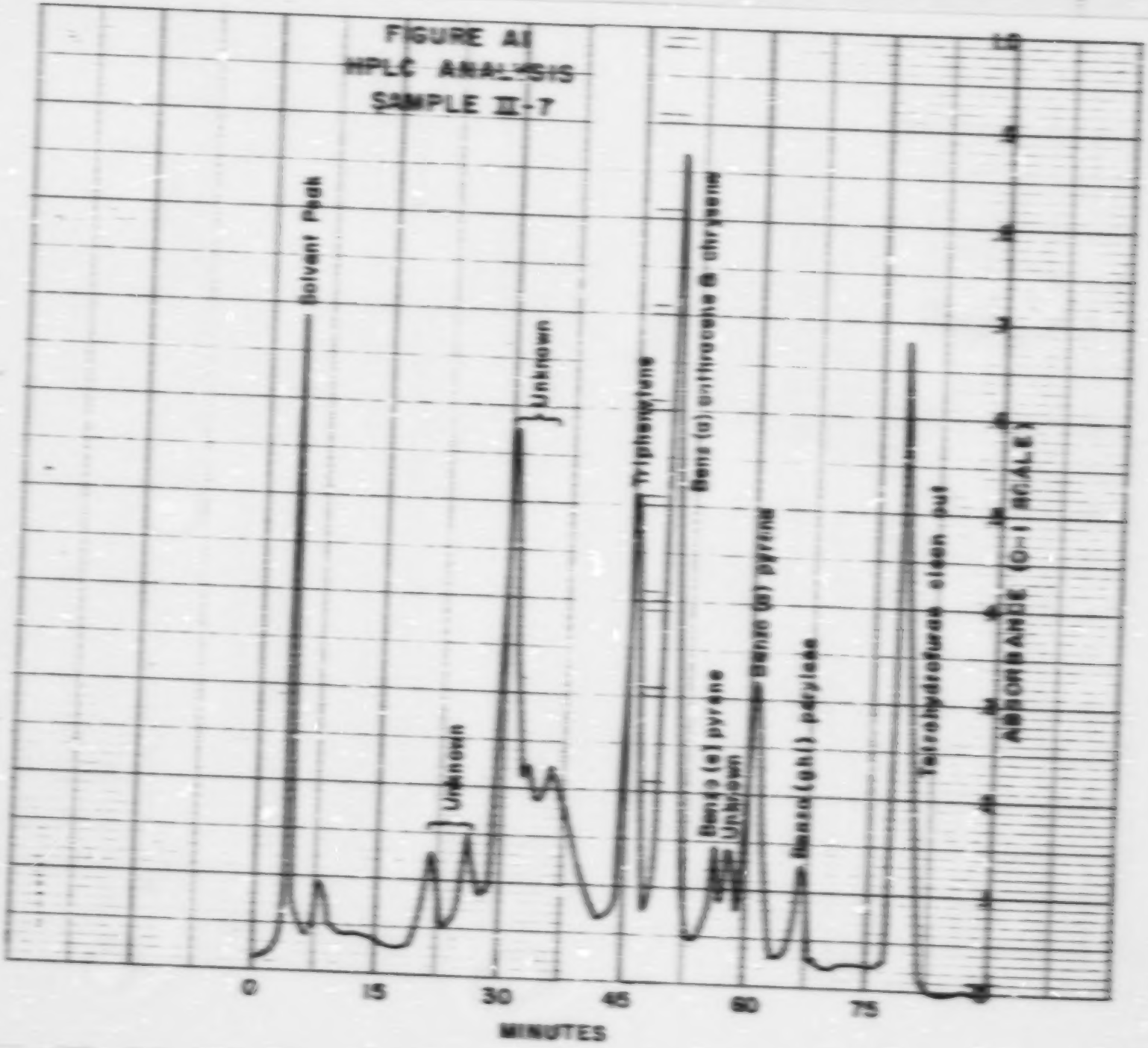


FIGURE A1
HPLC ANALYSIS
SAMPLE II-7
Solvent peak
Unknown
Triphenylene
Benzo (a) anthracene & chrysene
Benzo (e) pyrene
Unknown
Benzo (a) pyrene
Benzo (ghi) perylene
Tetrachlorinated oleon pal
ABSORBANCE (0.1 SCALE)
0
15
30
45
60
75
MINUTES

developed by a mobile phase consisting of ethanol, toluene and water (13:4:4, V/V/V). After developing, the fluorescent band of each desired compound is outlined, transferred by scraping directly into the nitrogen pressured filtering funnel and washed with hot methanol. The filter effluent is collected in 50 ml Erlenmeyer flasks and, after adding 1 ml n-hexadecane, evaporated to 1 ml. Three 10 ml portions of isooctane are added to the flasks with evaporation after each addition to remove all other solvents. The 1 ml n-hexadecane is transferred to a 1 cm ultraviolet cell and scanned for absorption in the 340-410 nm region. Identification and quantification are done by reference to previously prepared absorption spectra.

Liquid Scintillation Counting

Liquid scintillation counting is a highly sensitive and accurate technique for measuring the amount of radioactivity in samples containing radionuclides which emit low energy beta radiation such as compounds containing C^{14}. The technique involves preparing a "cocktail" containing a mixture of the sample material and a suitable scintillating solution. When beta rays from the radioactive material are absorbed in the scintillating solution, photons of light are emitted. The total number of light photons emitted in any one event is directly proportional to the energy of the absorbed beta ray. Each burst of photons initiated by the absorption of a beta ray is detected by a photomultiplier tube and the total number of output pulses from the photomultiplier tube is counted with an electronic scaling device. The voltage of each output pulse from the photomultiplier tube is proportional to the energy of the associated beta ray absorbed and may therefore be used for energy discrimination purposes. Instrument calibration is accomplished by counting a sample containing a known concentration of radioactive material and recording the sample counting rate. From this calibration standard, the efficiency of the instrument is determined which is defined as the ratio of counting rate to disintegration rate.

In order to determine the concentration of radioactivity in an unknown sample by the direct comparison with the calibration standard, it is necessary that the sample be composed of optically clear material in which none of the light photons are absorbed. In samples of cloudy material, some of the light photons are absorbed in the sample and are not detected by the photomultiplier tube. This phenomenon is called quenching and makes it necessary to apply a correction to the previously determined efficiency in order to accurately determine radioactivity in the sample. Quenching may also occur as the result of chemical characteristics of the sample.

Quenching effects may be taken into account in several different ways. One method is to spike the sample with a known quantity of additional radioactive material and to measure the change in total counting rate. In this manner, a calibration is determined for the specific matrix involved.

Another method of quenching correction is accomplished on the basis of voltage discrimination of the photomultiplier tube output pulse heights. In the normal counting of an unquenched sample, discriminators are set to bracket the region in which most of the pulses occur, i.e., maximum counting rate. In order to provide for quenching correction, a second set of discriminators is provided to accumulate the pulses in a separate and discrete region of the pulse height (voltage) curve. A quenching curve is then prepared by making a plot of counting efficiency as a function of the ratio of the counts in the two channels using a series of standards containing varying amounts of quenching. The quantity of radioactivity in an unknown sample is determined by reference to this curve.

PNA samples prepared by the methods described here have shown negligible quenching effects.

Additional background on solvents, equipment, alumina gel and the analysis of diesel fuels can be found in the First Annual Report.

APPENDIX B

DATA SUMMARY

Table B1 summarizes all of the engine runs completed on this project. Engine operating conditions, measured engine and exhaust gas parameters as well as PNA analyses are reported. Records were obtained for all the smoke cycles. Since smoke was not a prime objective of these experiments, these records were not processed. There was little variation in smoke from cycle to cycle based on visual inspection of the records.

Table B2 gives the inspection results for the fuel used during this study.

TABLE B1

ENGINE EXPERIMENTAL DATA

Engine Conditions	0:01 Hot/Cold Cycles	0:10 Hot/Cold Cycles	0:20 Hot/Cold Cycles	0:30 Hot/Cold Cycles	0:31 13-Mode[1]	1:1 13-Mode	1:2 13-Mode	1:3 Hot/Cold Cycles	1:6 Hot/Cold Cycles	1:9 13-Mode	1:6 13-Mode Diesel
Total Sample, m^3											
Dilution Ratio(Air/Sample)											
Exhaust Sample, m^3	7.05	7.10	7.10	7.07	7.10	7.07	7.09	7.02	7.72	7.05	8.01
Total Engine Exhaust, m^3	721	703	700	706	729	906	1050	814	937	1010	910
Ratio Exh./Sample	29.6	100.1	100.7	111.1	107.1	100	130.6	100.1	121.1	130.0	113.1
Fuel Consumption, kg	23.5	20.1	27.0	26.0	16.1	15.1	18.0	21.1	20.6	15.1	16.1
Test Time, Hr:	1.71	1.58	1.88	1.50	1.00	2.17	2.11	1.20	1.50	2.17	2.17
SHP					11.10	11.71	11.90			10.20	17.10
Sample System[2]	A	A	A	A	A	A	A	A	A	A	A
Exh.Temp.Before Precooler,°C	165-1001	161-1001	160-1001	159-1001	82-1001	85-1001	83-620	196-327	191-355	82-166	-
Exh.Temp.After Precooler,°C	47-168	50-158	52-161	50-158	49-171	46-210	49-160	85-201	52-170	46-159	-
Diluted Exh. Temp., °C											
Exhaust Gas Components:											
O_2, %					14.6	13.6	13.5			17.6	17.9
CO, %					0.006	0.071	0.011			0.002	0.015
CO_2,%					3.9	5.1	5.2			3.4	3.4
HC, ppm					151	531	661			351	109
NO, ppm					600	816	829			864	705
NO$_2$, ppm					453	1103	1081			1027	937
NH_3, ppm											
CO_2 Diluted, %											
NO, Diluted, ppm											
Smoke, % Opacity[3]	10.1(A) 15.2 (B) 35.1 (C)	(5)	(5)	(5)				13.5 (A) 9.5 (B) 20.7 (C)	(5)		
Analytical Results:											
Analytical Schedule[5]	A	A	A	A	A	A[6]	A	A	A	A	A
Tracer Added, ug[7]	0	0	0	0	0	0	0	0	0	0	0
DeP	0.11	0.11	0.11	0.11	0.11	0.22	0.11	0.11	0.11	1.37	1.20
DeA											
Tracer Recovered, ug											
DeP	.011	.061	.035	.010	.025	.070	.022	.066	.00075	.010	.102
DeA											
Correction Factor											
DeP	10.	1.7	3.1	2.9	5.5	2.9	5.0	2.5	145.	72.	12.5
DeA											
Total PNA (TN), ug											
DeP	0.01	0.56	0.10	2.07	0.07	0.11	0.08	0.09	0.01	0.10	0.21
DeC	ND	0.10	ND	ND	0.20	ND	0.57	0.12	0.50	1.67	0.16
DeA	ND	ND	ND	ND	ND	ND	0.21	0.17	0.13	0.53	0.21
DeP	ND	0.11	0.12	ND	0.17	ND	ND	0.04	0.02	0.10	0.12
DeA/P											
Engine Exh. Flow Rate, Difference											
DeP	.01	.00	.01	.01	.05	.05	.06	.06	.01	.00	.11
DeA											
Corrected Eng. Yield, ug											
DeP	.10	1.00	.22	.09	.26	.15	.00	.11	1.15	1.0	1.4
DeA											
ug/m^3 Exhaust											
DeP	.007	.150	.030	.013	.033	.019	.020	.015	.100	.100	.15(10)
DeA	ND	1.27	ND	ND	.020	ND	.034	.063	.052	.210	.01(10)
DeC	ND	ND	ND	ND	ND	ND	.020	.022	.017	.071	.06(10)
DeP	ND	.102	.017	ND	.016	ND	ND	.005	.005	.016	.01(10)
DeA/P											
ug/kg Fuel											
DeP	.00	5.11	.70	.10	1.00	.24	.00	.22	7.05	22.0	.0035
DeC	ND	37.1	ND	ND	1.27	ND	1.00	.00	.00	6.63	.0067
DeA	ND	ND	ND	ND	ND	ND	.76	.15	.15	2.00	.0120
DeP	ND	2.00	.50	ND	1.00	ND	ND	.08	.06	.61	.0037
DeA/P											
ug/BHP-Hour											
DeP					0.10	0.10	0.13			1.35	.0020
DeC					0.11	ND	0.63			1.22	.0066
DeA					ND	ND	0.16			0.50	.0021
DeP					0.27	ND	ND			0.08	.0007
DeA/P											

See page with all footnotes for Table B1.

Engine Conditions	1:7	1:8	1:9	1:10	1:11	1:12	1:13	1:14	1:15	1:16	1:17
	13-Mode	Cycles	1800 RPM 17% Load	1800 RPM 17% Load	1800 RPM 17% Load	13-Mode	1800 RPM 17% Load	1800 RPM Full Load	1800 RPM Full Load	1800 RPM Full Load	1800 RPM Full Load
Total Sample, m^3	-	-	37.9	35.8	36.7	37.6	117	60.5	59.9	60.8	60.5
Dilution Factor(DF)/Sample	-	-	6.0	6.0	6.0	6.0	1.0	1.93	2.96	2.01	1.19
Exhaust Sample, m^3	7.03	7.18	5.90	5.11	5.33	5.51	58.63	2.98	14.03	11.72	11.11
Total Engine Exhaust, m^3	980	830	1180	1020	1065	1010	6857	1981	2130	1910	1892
Basis Exh./Sample	140.0	116.0	197.1	170.0	177.3	161.2	99.0	130.	213.	211.	184.
Fuel Consumption, kg	14.0	11.8	17.4	12.0	11.0	10.0	170.1	21.0	115.0	20.0	20.0
Test Time, Hr.	1.33	1.15	1.75	1.03	1.03	1.00	11.60	1.00	1.07	1.00	1.00
DEP	07.00	-	04.07	04.00	00.07	01.77	00.02	210.00	204.01	007.00	110.11
Sample System[1]	1	1	1	1	1	1	1	1	1	1	1
Exh.Temp.Before Precenter,°C	72-106	103-201	-	-	-	21-140	-	110	100	100	171
Exh.Temp.After Precenter,°C	61-100	68-100	75-170	80-170	90-105	91-100	93-121	201	211	255	149
Diluted Exh. Temp., °C	-	-	4.16	0.20	10.11	17.11	27.10	27	29	29	20
Exhaust Gas Components:											
O_2, %	13.0		-	-	-	11.1	-	0.0	0.7	0.1	0.7
CO, %	0.201		-	-	-	0.200	-	0.170	0.004	0.071	0.001
CO_2, %	1.0		0.7	0.0	0.7	5.1	0.0	0.7	0.7	1.0	0.7
HC, ppmC	205		-	-	-	151	-	252	254	271	204
NO, ppm	830		-	-	-	700	-	-	-	1101	1551
NO_x, ppm	844		-	-	-	1011	-	1042	1570	-	-
CO_2 Diluted, %	-		1.21	1.00	1.00	-	0.00	2.0	2.1	2.1	2.1
NO_x Diluted, ppm	-		-	-	-	-	-	1.2	1.2	1.2	1.1
Calc. % Aperilp[1]	-	151	-	-	-	-	-	-	-	-	-
Analytical Results:											
Analytical Bridge[1]	1	1	1	1	1	1	1	1	1	1	1
Tracer Added, mg[1]	1	1	1	1	1	1	1	1	1	1	1
Dif	1.01	1.11	1.25	1.00	1.23	1.21	1.24	1.19	1.21	1.21	1.17
Dup	-	-	1.07	1.01	-	1.15	13.54	1.07	1.24	1.24	1.17
Tracer Recovered, mg[1]											
Dif	.000	.0030	.14	.12	.11	.119	.13	.05	.12	1.21	1.12
Dup	-	-	.16	.14	.11	.17	1.54	.05	.06	1.21	1.14
Correction Factor											
Dif	19.	104.	1.1	1.09	1.11	1.1	1.1	10.	10.	1.21	1.11
Dup	-	-	1.0	1.10	1.14	1.1	1.1	10.	10.	1.21	1.11
Total PAH (IR), mg											
Dif	0.11	.01	0.07	0.07	0.11	0.11	1.07	0.11	0.10	1.10	0.10
Dup	0.09	.11	1.00	1.11	1.14	1.13	15.06	0.11	0.11	1.11	0.12
Dup	0.13	.14	0.06	0.01	0.11	0.12	0.01	0.11	0.11	1.11	0.12
Ophib	0.00	.01	0.11	0.11	0.17	0.10	1.11	.01	0.04	0.04	0.14
mg/kg Fuel											
Dif	0.07	.01	0.12	0.11	0.11	0.10	1.01	1.12	0.11		
Dup	-	-	2.11	2.11	2.14	1.11	13.54	1.06	0.14		
Corrected Dig. Visib. mg											
Dif	1.1	.10	1.11	.99	.93	1.11	111.	1.1	1.		
Dup	-	-	0.16	1.11	0.10	0.11	10.	1.1	1.		
mg/m³ Outside											
Dif	.101	1.1	.117	.102	.110	.111	.01	.11	.1		
Dup	.111	.104	1.100	.021	1.11	0.11	1.14	.1	.01		
Dif	.101	.011	.000	.121	.111	.101	.111	.011	.001		
Ophib	.011	.000	.100	.104	.110	.111	.112	.101	1.000		
mg/kg Fuel											
Dif	1.11	.11	11.1	1.1	1.11	11.1	10.1	11.1	101.		
Dup	1.01	.01	11.1	11.1	11.1	11.1	10.1	1.1	11.1		
Dup	1.01	.11	1.11	1.11	1.11	.11	1.11	1.11	1.11		
Ophib	.10	.01	1.00	1.11	1.11	.11	1.11	0.11	0.14		
mg/BHP-Hour											
Dif	1.11	-	1.11	.11	1.11	1.11	11.10	1.11	10.11		
Dup	0.10	-	1.11	1.00	1.11	1.11	1.11	1.11	1.11		
Dup	0.11	-	0.11	0.11	0.10	1.11	1.11	0.11	0.11		
Ophib	0.01	-	0.11	0.10	0.11	0.11	0.11	0.111	0.11		

See page with all footnotes after Table B1.

TABLE B1 CONTINUED

ENGINE EXPERIMENTAL DATA

Engine Conditions	B1:5 1000 RPM Full Load	B1:6 1000 RPM Full Load	B1:7 1000 RPM Full Load	B1:8 1000 RPM 0 Load	B1:9 1,400 RPM 0 Load	B1:10 1400 RPM ¼ Load	B1:11 1400 RPM ½ Load	B1:12 1400 RPM ¾ Load	B1:13 1400 RPM Full Load	B1:14 1800 RPM Full Load	B1:15 1800 RPM Full Load	B1:16 1800 RPM Full Load
Total Sample, g[1]	61.0	0.84	58.3	61.0	61.0	60.3	0.10	10.03	60.0	10.0	60.0	20.1
Dilution Ratio (Air/Sample)	5.36	5.10	19.3	3.79	3.81	3.91	1.52	3.09	3.15	5.00	3.10	1.0
Exhaust Sample, g[2]	9.65	2.93	9.09	10.93	10.63	9.19	3.99	5.33	0.00	9.96	0.92	6.91
Total Engine Exhaust, g[3]	1653	660	1781	739	741	803	183	599	857	814	857	540
Ratio Exh./Sample	131	150	773	88.3	89.6	90.3	83.8	91.3	183	183	188	154
Fuel Consumption, kg	69.6	15.3	78.6	18.3	18.9	9.19	1.19	13.7	30.9	30.9	30.9	15.0
Test Time, Hr.	0.00	0.60	0.00	0.00	0.00	1.00	00	1.00	1.00	1.00	1.00	1.00
BSFC	201.93	611.59	210.01	15.39	15.03	15.06	15.11	93.99	203.0	233.2	203.0	234.6
Sample System[5]	5	0	0	7	5	0	0	3	5	3	5	5
Exh. Temp Before Dilutor, °C	360	356	399	154	158	154	111	139	188	196	201	191
Exh Temp After Dilutor, °C	230	350	81	91[6]	111	136	36	139	211	209	210	212
Dilutor Exh. Temp., °C	36	51	31	33	31	38	19	17	27	29	26	25
Exhaust Gas Components:												
O_2, %	0.0	0.0	0.1	17.0	17.0	17.0	17.5	11.3	0.0	0.0	0.1	0.0
CO, %	0.001	0.000	0.015	0.001	0.000	0.000	0.000	0.003	071	001	031	001
CO_2,%	0.0	0.0	0.0	2.0	1.0	0.0	0.7	5.9	0.1	0.1	0.1	1.1
HC, ppm	000	000	071	000	000	010	010	000	761	200	276	217
NO, ppm	1933	1501	1000	271	251	001	101	1190	1300	1361	1291	1400
NO_2, ppm	-	1710	1000	101	110	361	150	1000	1610	1130	1000	1101
CO_2 Diluted %	0.0	0.0	-	-	0.000	0.001	0.011	2.0	0.0	0.1	0.1	2.01
NO_x Diluted, ppm	-	-	00	100	01	01	110	101	117	117	200	111
Smoke, % Opacity[9]	0.1	0.0	0.0	011	011	011	011	0.0	0.0	0.0	0.0	1.0
Analytical Results:												
Analytical Driving[9]	0	0	0	0	0	0	0	0	0	0	0	0
Tracer Added, µg[11]	0	0	0	0	0	0	0	0	0	0	0	0
Ref	0.93	0.92	1.00	1.11	1.01	1.05	1.00	1.02	1.00	1.07	1.00	1.11
Bag	0.00	0.96	1.00	1.11	1.01	1.05	1.00	1.02	1.00	1.07	1.00	1.11
Tracer Recovered, µg[12]												
Ref	1.00	1.12	22	00	12	27	03	07	001	000	1.00	21
Bag	1.01	1.06	00	01	10	07	03	07	010	202	1.00	21
Correction Factor												
Ref	1.1	1.0	10.0	10.0	11.0	1.1	1.1	1.1	11.1	11.0	1.1	1.1
Bag	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.11	0.0	1.1	1.1
Total PMS (Dil. µg												
Ref	1.00	1.12	0.02	0.10	0.10	0.11	1.01	0.01	10	10	1.00	1.21
Bag	0.0	00	0.00	0.11	0.10	0.10	0.11	00	10	11	1.25	1.21
Ref	00	00	0.00	0.11	0.11	0.10	0.11	0.11	10	11	1.25	1.21
Bg/Bf	00	00	0.00	0.11	0.11	0.10	0.11	0.11	10	11	1.25	1.21
Engine Out												
(By difference)												
Ref			0.01	1.01	1.01	1.01	1.01	1.01	10	11	1.01	1.1
Bag			0.01	1.01	1.01	1.01	1.01	1.01	10	11	1.01	1.1
Corrected Eng. Visib. ug												
Ref			00	1.00	1.00	1.00	1.00	1.01	1.01	1.00	1.11	1.11
Bag			00	1.00	1.00	1.00	1.00	1.01	1.01	1.00	1.11	1.11
g/m³ Exhaust												
Ref			21	00	11	11	11	11	11	11	11	10
Bag			21	11	11	11	11	11	11	11	11	10
Ref			010	010	010	011	010	11	01	01	01	01
Bg/Bf			010	011	010	011	010	11	01	01	01	01
g/kg Fuel												
Ref			0.1	10.1	10.0	11.1	11.1	11.1	11.1	11.1	11.1	1.1
Bag			0.1	11.1	11.0	11.1	11.1	11.1	11.1	11.1	11.1	1.1
Ref			0.1	1.1	1.1	1.1	1.1	11	11	11	1.1	1.1
Bg/Bf			0.1	0.0	1.1	1.1	1.1	11	11	11	1.1	1.1
g/BHP-Hour												
Ref			1.11	1.00	1.00	11.11	1.11	1.11	1.11	1.11	1.11	1.1
Bag			1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.1
Ref			0.11	0.11	0.11	1.11	1.11	11	11	11	1.11	1.1
Bg/Bf			0.11	0.11	0.11	1.11	1.11	11	11	11	1.11	1.1

see page with all footnotes after table B1

FOOTNOTES FOR TABLE XI

(Engine Experimental Data)

*Weight based on radioactive count.

ND = Not Detected.

(1) 13-mode cycle runs were made by adjusting the time for each mode to compensate for the different exhaust flow rates while sampling at a constant flow rate. The test time listed is the actual test time while the total engine exhaust and fuel consumption are calculated as if the standard 130-minute run were made. The BHP and average gaseous emissions were calculated by the standard 13-mode weighting factors.

(2) a = Sample system 1.
b = Sample system 2.
c = Sample system 2 without $CaCl_2$ trap.
d = Sample system 3 no air flushing.
e = Sample system 3 with 1/2 hr. air flush at 10m^3/hr. at room temperature.

(3) a = Acceleration mode.
b = Lugging mode.
c = Peaks in either mode.

(4) Smoke data available but not processed.

(5) a = Original analysis scheme, Soxhlet extraction with methanol-benzene overnight.
b = HPLC step added for all future runs.
c = Soxhlet extraction shortened to 8 hrs.
d = Methanol-benzene changed to pure benzene in extraction.
e = Soxhlet extraction shortened to 4 hrs.
f = An additional 8-hour re-extraction.
g = Soxhlet extraction for 2 hours with benzene followed by a 3-hour re-extraction with benzene.

(6) The sample extract for this run was divided into two equal samples with one being analysed initially and the other 4 days later. The total results are reported.

(7) a = Tracer added to solution after Soxhlet extraction.
b = Tracer added to solvent prior to Soxhlet extraction.
c = Tracer injected into the exhaust sample.
d = Tracer injected onto the filter containing soot.
e = Same as d but with soot first flushed with ammonia.
f = Tracer injected onto a clean filter and protected from soot during run.
g = Tracer injected onto a clean filter prior to engine run.
h = Tracer added to soot sample prior to Soxhlet extraction.
i = Tracer added to soot sample prior to extraction and isooctane injected into sample stream.

(8) Total blowby was sampled in this run. Values for ug/m^3 exhaust are ug/m^3 of blowby.

TABLE B2

TEST FUEL INSPECTION DATA

	Composite No. 2 Fuel From 10 Mfgs.
API Gravity	36.9
Density	.8435
Cetane Index	50
FIA	
Aromatics	26.0
Olefins	0.9
Sulfur: %	0.17
Distillation: °F.	
10%	417
50%	498
90%	589
PNA Content ug/kg	
BaP	41
BaA	108
BeP	75
BghiP	26
Chrysene	72
Triphenylene	35
Pyrene	144
Fluoranthene	869